

RESEARCH ARTICLE | APRIL 18 2007

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M. Cocchi; J. Kalinowski; D. Virgili; V. Fattori; S. Develay; J. A. G. Williams



Appl. Phys. Lett. 90, 163508 (2007)


<https://doi.org/10.1063/1.2722675>



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Single-dopant organic white electrophosphorescent diodes with very high efficiency and its reduced current density roll-off

M. Cocchi^{a)}

Institute of Organic Synthesis and Photoreactivity, National Research Council of Italy (ISOF-CNR), I-40129 Bologna, Italy

J. Kalinowski^{b)}

Department of Molecular Physics, Gdańsk University of Technology, 80-952 Gdańsk, Poland

D. Virgili and V. Fattori

Institute of Organic Synthesis and Photoreactivity, National Research Council of Italy (ISOF-CNR), I-40129 Bologna, Italy

S. Develay and J. A. G. Williams

Department of Chemistry, University of Durham, DH1 3LE Durham, United Kingdom

(Received 21 February 2007; accepted 14 March 2007; published online 18 April 2007)

Very high-efficiency organic white light electrophosphorescent diodes (WLEDs) have been fabricated using an efficient N[^]C[^]N-coordinated platinum (II) complex phosphor dopant. Their white light emanation is underlain by the simultaneous emission of monomer in blue and excimer in red. By optimizing the phosphor concentration and confining the electron-hole recombination zone to the emitter layer in the devices, the authors achieve their unusually high forward viewing external quantum efficiency (QE) up to 15.5±0.2% and 13.0±0.2% photons/electron at low and high drive current densities, corresponding to 40 and 1300 cd/m², respectively. The current density where QE drops by half of its peak value is greater than three times that of the highest efficiency single-dopant WLEDs reported hitherto. The performance parameters of the presented devices can be further improved by using efficient dopants with the emission spectrum shifted towards blue.

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Organic white light emitting diodes (WLEDs) have attracted a great deal of attention due to their potential applications as lighting sources that are less expensive and more efficient than conventional incandescent and fluorescent illumination sources.^{1,2} There are several routes to cover the visible spectrum uniformly by emission from WLEDs. An obvious approach is to use a stacked² or multilayer^{3,4} light emitting diode (LED) structure with three separate emitters, that is, blue, green, and red, though three emitters can be mixed together in a single layer to achieve white emission.⁴⁻⁶ Another more promising approach is to use a combination of only two dopants with substantially different electron affinities (electron donor-acceptor systems). The combination of acceptor-located electrons with donor-located holes yields a broadly emitting exciplex, i.e., an excited state of a complex of two dissimilar molecules.⁷ In that case we deal with exciplex light emitting diodes (EXLEDs). Their reported external electroluminescence (EL) quantum yields currently do not exceed 1% photons/electron (ph/e).⁸ However, experiments with organic phosphor dopants reveal a possibility to improve the EXLEDs' performance.⁹ One of the most promising routes to improve the WLED efficiency seems to be the use of only a single dopant in the emissive layer^{10,11} that emits simultaneously from monomer states (in blue) and excimer states (in red). An excimer is a two-molecule complex of the same compound, which is bound only in the excited state and rapidly dissociates to two separate molecules (monomers) after relaxation to the ground

state.⁷ As reported only recently, such monomer/excimer emitting WLEDs have revealed very high forward viewing external quantum efficiencies (QEs) up to ≅15.9% ph/e around the brightness of 500 cd/m².¹²

In this letter, we demonstrate that, following this route with a highly efficient phosphor dopant and through judicious engineering of the WLED structure, not only such an unusually high external EL QE can be obtained (up to 15.5% ph/e at a brightness of ≅40 cd/m² and up to 13% ph/e at a brightness of 1300 cd/m²), but a remarkable reduction in the high drive current density roll-off of QE can also be achieved. The drive current density where QE declines by half of its peak value is greater than three times that of the highest efficiency single-phosphorescent dopant WLEDs.¹²

We have chosen a monomer/excimer emitting dopant PtL²Cl (Fig. 1) from a group of highly efficient N[^]C[^]N-coordinated platinum (II) complex phosphors, PtLⁿCl (where n=1-6 represents various substituents at the 4 position of the central phenyl ring, CO₂Me for L²),¹³ and fabricated a four-layer LED. The performance of the emissive layer has been optimized by doping the PtL²Cl into a CBP:OXA mixture, which has good transporting properties for both holes and electrons, and by locating it between exciton blocking layers of CBP and OXA; the latter acting also as an electron-transporting and hole-blocking layer. A hole-transporting compound TPD (75 wt %) has been blended with the PC binder (25 wt %) to prevent molecular diffusion and crystallization. The LED architecture is shown in the inset of Fig. 1, where its EL spectra are shown along with the monomer and excimer photoluminescence (PL) spectra. WLED devices were prepared with the general structure in-

^{a)}Electronic mail: cocchi@isof.cnr.it

^{b)}Electronic mail: kalino@polnet.cc

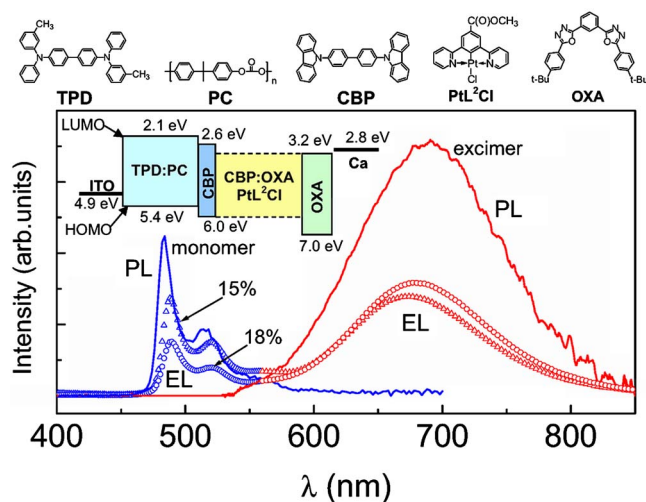


FIG. 1. (Color online) Normalized monomer (left point curves) and excimer (right point curves) EL spectra at two different PtL^2Cl concentrations of the device shown in the inset. Indicated are the lowest unoccupied molecular orbital energies and the highest occupied molecular orbital energies of the materials used. Top: The molecular formulas of TPD [*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine], PC (bisphenol-A-polycarbonate), CBP (4,4'-*N,N'*-dicarbazole-biphenyl), PtL^2Cl [platinum II[methyl-3,5-di(2-pyridyl) benzoate]chloride] and OXA {3,5-bis[5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl]-benzene}. The PL spectra of low-doped (5%) samples and a 100% evaporated PtL^2Cl film are shown for comparison (solid lines).

dium tin oxide (ITO)/TPD:PC (80 nm)/CBP (30 nm)/CBP:OXA: PtL^2Cl (80 nm)/OXA (30 nm)/Ca (for chemical names and molecular structures see Fig. 1). The composition of the emitter layer CBP:OXA: PtL^2Cl varied between 47:47:6 and 25:25:50 by weight.

The synthesis of the PtL^2Cl phosphor used is described in detail elsewhere.¹⁴ Other compounds purchased from Aldrich (TPD), Syntech (OXA), and Polysciences Inc. (MW = 32 000–36 000 PC) were used as supplied. CBP was kindly provided by Syntech. Solution photophysical characterization of the materials was carried out using a Jobin-Yvon Fluoromax 2 spectrofluorimeter and a *Q*-switched Nd:YAG-pumped system with a Hamamatsu R928 photomultiplier tube for the determination of lifetimes. Solid state absorption and emission measurements were made using a Perkin Elmer Lambda 9 UV/v is/near IR spectrometer and a StellarNet spectroradiometer, respectively, and a single-photon IBH model 5000 counter was employed for the time-resolved luminescence measurements. Devices were fabricated by spin coating the first layer on an ITO glass substrate (20 Ω /square) and then vacuum depositing the overlying layers at a pressure of 0.05 mPa. The evaporation rate of CBP and OXA layers was 0.2 nm/s, while the deposition rate of the emitter layer from a mixture of (CBP:OXA: PtL^2Cl) was 2 nm/s. Each layer thickness was measured with a Tencor Alpha Step 200 profilometer. The current-voltage characteristics were measured with a Keithley source-measure unit, model 236, under continuous operation mode, while the light output power was measured with an EG&G power meter. All measurements were carried out at room temperature under argon atmosphere and were reproduced for many runs, excluding any irreversible chemical and morphological changes in the devices.

The PL spectrum with a dominating blue monomer emission band peaking at 490 nm is characteristic of low

doping level ($\leq 6\%$) emitters (almost no excimerlike emission is apparent). As the PtL^2Cl doping concentration in the emitter is increased, we observe both strong monomer and excimer emissions. At still higher doping level, a gradual reduction of the monomer component of the emission is observed and a 100% PtL^2Cl film shows only the red emission emanating from the radiative decay of the excimers (see Fig. 1). The emission single-exponential decay kinetics registered in argon for a 6% doped emitter film yields the phosphorescence time of 5.3 μs , which is comparable with that measured in dilute dichloromethane solution, 7.8 μs at infinite dilution.^{13,14} This similarity suggests that, under these conditions in the matrix, the platinum complex guest behaves as an isolated excited molecule and its PL quantum efficiency in the film (monomer emission component) must be comparable to the high value found in solution, $\varphi_{PL}(\text{monomer}) = 0.58$.^{13,14} The emission decay kinetics registered in argon within the 650–700 nm range for a 100% PtL^2Cl vacuum-evaporated film exhibits a monoexponential behavior with 1.1 μs as the lifetime of the emitting species. We measured the excimer PL and EL efficiencies in a 100% doped film: $\varphi_{PL}(\text{excimer})$, which, though lower than $\varphi_{PL}(\text{monomer})$, still appear to be as high as 35% and φ_{EL} as high as 10% ph/e.¹⁵

The devices reveal EL spectra consistent with the dopant PL spectrum (Fig. 1). The PtL^2Cl excimer is formed after the exciton is localized on the molecule (via energy transfer from CBP to PtL^2Cl monomer or hole-electron recombination at PtL^2Cl molecules). The excimer-to-monomer component emission ratio (thus, the WLED color) is a function of the dopant concentration and becomes larger at higher doping levels. White light from a balance of monomer and excimer emissions is observed for devices with PtL^2Cl doped emitters between 10 and 20 wt %. The EL spectra at two concentrations from this range are presented in Fig. 1. The ratio of monomer/excimer contributions is quasi-invariant with applied voltage, leading to a reasonable quality white emission. The CIE coordinates $x=0.43$ and $y=0.43$ for the 15% doped device are close to those found in an incandescent lamp, approximately $x=0.41$ and $y=0.41$ (see Fig. 2). At a higher concentration (18%), the CIE coordinates (0.47, 0.41) are shifted to the red as compared with those for incandescent lamps. The peak brightness at ≈ 80 mA/cm² of the 15% doped device was ≈ 7000 cd/m² and the maximum quantum efficiency was $15.5 \pm 0.2\%$ ph/e (14.2 ± 0.2 cd/A) at 10 cd/m², showing only a slight drop to $13.5 \pm 0.2\%$ ph/e (12.6 ± 0.2 cd/A) at 1000 cd/m². While the brightness and maximum external EL QE are comparable with the best reported data for single-dopant WLEDs,^{11,12} here, the high current density roll-off in QE remarkably weakens. The emission efficiency of two of the single-dopant WLEDs with two different concentrations of PtL^2Cl versus current density is shown in Fig. 3. The quantum efficiency decreases at high current densities, however, the decrease is less severe than in most other electrophosphorescent devices,^{16,17} including single-dopant WLEDs.^{10,12,18} Less than 50% drop of the maximum EL quantum efficiency at 100 mA/cm² is observed, while as high as three- to fourfold roll-off was found for the most efficient single-dopant WLEDs reported hitherto.^{12,14,18} This is a notable advantage of the present WLEDs, resulting from the reduced sensitivity of emissive states to quenching by their mutual interaction,^{4,16} fate on charge carriers,^{7,16,17} and electric-field-enhanced dissociation.^{7,17}

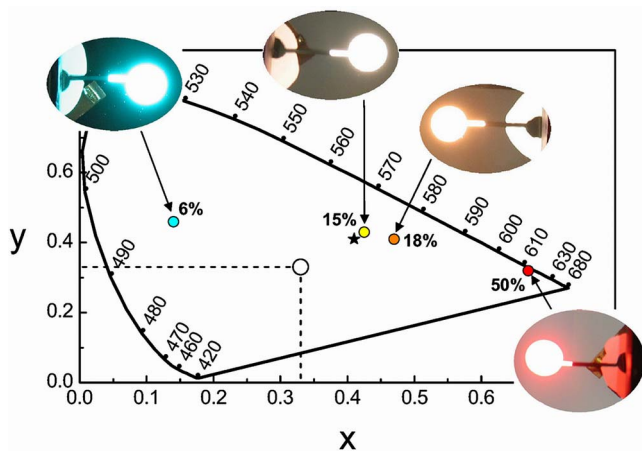


FIG. 2. (Color online) CIE chromaticity diagram for the device ITO/TPD:PC/CBP/CBP:OXA: x PtL₂Cl/OXA/Ca. The blue monomer emission (left top) and red excimer emission (right bottom) for a device doped at $x=6\%$ and $x=50\%$ of PtL₂Cl, respectively, the combined monomer+excimer emission for devices doped at 15% and 18% (right top). The dots refer to the color points of the emission spectra of the devices with different concentrations of PtL₂Cl. Concentrations close to 15% gave the CIE coordinates closest to white (0.33, 0.33) (open circle) and those found in incandescent lamp (approximately 0.41, 0.41) (asterisk).

In summary, we have demonstrated that single-dopant fully electrophosphorescent organic WLEDs can take advantage of the effective formation of highly emissive excimers to produce bright white devices with very high quantum and

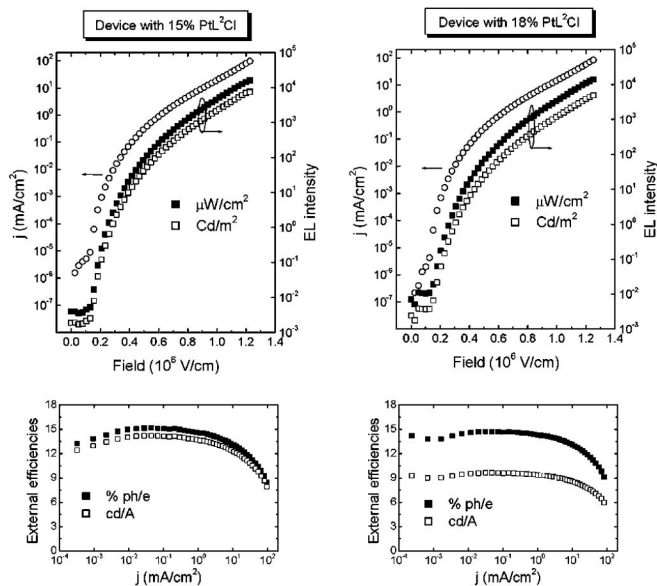


FIG. 3. WLED device electro-optical properties for two different concentrations of the PtL₂Cl phosphor. The photon (ph) energies have been averaged over the complete emission spectra and Lambertian intensity profiles have been assumed in the calculation of the external quantum efficiency (% ph/electron) of each device.

luminous efficiencies. The device color and its performance parameters can be tuned by varying the dopant concentration in the emitter layer and by its architecture, introducing excitation blocking layers between hole- and electron-transporting layers. The high performance, including a substantial reduction in the high drive current density QE roll-off, of the presented LEDs is attributed to the high radiative relaxation rate of PtL₂Cl excimers and the LED structure confining the emission zone to the emissive layer. Experiments are currently underway to improve the performance parameters of the present devices by using efficient phosphor dopants with the full emission spectrum shifted towards blue and by optimizing the device architecture to increase its power efficiency. The simple device structures make them well suited to low cost lighting applications. We expect that these device structures¹⁹ will have several benefits over stacked² or multiple doped single emissive layer devices.^{5,6}

This work was supported by MIUR-FIRB Project No. RBNE019H9K, CNR Project No. PM-P04-010 (MACOL), and European COST Project No. D35-0010-05.

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